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## Particle Growth of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ with $x \leq 0.2$ by Air Oxidation of Aqueous Suspensions

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The conditions were studied for promoting the particle growth of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  with  $x \leq 0.2$  by oxidation with air at  $70^\circ\text{C}$  of  $\text{Fe}(\text{OH})_2$  suspensions containing slight amounts of  $\text{Co}(\text{II})$ . The particle growth by oxidation is accelerated notably with increasing concentrations of both excess  $\text{NaOH}$  and  $\text{Fe}(\text{II})$  in the starting suspension. The presence of extremely fine  $\text{Fe}_3\text{O}_4$  particles in the starting suspension retards the particle growth by oxidation. The samples consist of multi-, single-, and sub-domain (or superparamagnetic) particles, each being inhomogeneous in  $\text{Co}(\text{II})$  concentration, with their intermingled particle ratio as well as the inhomogeneity as governed by the conditions for the particle growth.

KEY WORDS: Air oxidation/ Particle growth/ Cubic particle/ Single-domain particle/ Coercivity/  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ /

The precipitates consisting of cubic  $\text{Fe}_3\text{O}_4$  particles can be prepared by oxidation of  $\text{Fe}(\text{OH})_2$  suspensions, provided that the conditions for oxidation are suitably chosen. The appropriate conditions of oxidation have been investigated for the formation of  $\text{Fe}_3\text{O}_4$ .<sup>1)</sup> The temperature at which  $\text{Fe}_3\text{O}_4$  is formed is lowered with decreasing concentration of either excess  $\text{NaOH}$  or iron (II) salt in the starting suspension, whereas each concentration range suitable for the formation of  $\text{Fe}_3\text{O}_4$  becomes wider with increasing oxidation temperature beyond  $50^\circ\text{C}$ . The  $\text{Fe}_3\text{O}_4$  samples with greater than  $0.01 \mu\text{m}$  in mean particle sizes could successfully be prepared by selecting the oxidation conditions, and their magnetic properties were dependent on the particle sizes. It has been well known that the substitution of slight amounts of  $\text{Co}(\text{II})$  for  $\text{Fe}(\text{II})$  in  $\text{Fe}_3\text{O}_4$  causes a magnetically harder material. The precipitates of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  with  $0.05 \leq x \leq 0.2$  were also prepared in the presence of slight amounts of  $\text{Co}(\text{II})$  under oxidation conditions similar to those for  $\text{Fe}_3\text{O}_4$  formation.

This paper deals with oxidation conditions for the growth of particles of the compositions of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  with  $x \leq 0.2$  and their magnetic properties.

### EXPERIMENTAL

The starting suspension, varying in the concentrations of iron(II) and excess  $\text{NaOH}$ , were prepared as follows: Acidic solutions containing different concentrations of  $\text{Fe}(\text{II})$  were prepared by dissolving  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (both of analytical grade) in water. To every 1 L (1 L = 1 dm<sup>3</sup>) solution, a  $\text{NaOH}$  solution whose

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concentration had been suitably controlled was added in various  $2\text{OH}^-/\text{Fe(II)}$  ratios ( $R$ ). Each suspension was diluted with water to 3 L in a 4 L flask. The oxidation of each 3 L suspension was carried out at  $70^\circ\text{C}$  by bubbling  $\text{CO}_2$ -eliminated air into at a constant rate of 300 L/h. The construction of the flask for the air-oxidation experiments has previously been described.<sup>1)</sup>

To investigate the transformation into  $\text{Fe}_3\text{O}_4$  in the course of oxidation, a 40–50  $\text{cm}^3$  sample was taken several times from each suspension during oxidation. After sampling each filtered precipitate in muddy form was subjected to X-ray, electron microscopic, and chemical examinations. Oxidation for the suspensions with  $R \leq 1$  was stopped when the pH dropped sharply with the disappearance of dark blue (or green) or whitish precipitate in the suspension, whereas the alkaline suspensions with  $R > 1$  were oxidized until  $\text{Fe(OH)}_2$  was completely oxidized. A number of alkaline suspensions were also prepared by using acidic solutions containing  $\text{Fe(II)}$  and either of  $\text{Fe(III)}$  or  $\text{Co(II)}$ .

The oxidation products were filtered, washed with water, and treated with acetone. The black slurries prepared by oxidation in the absence or presence of  $\text{Fe(III)}$  in the starting suspensions were, respectively, dried at  $70^\circ\text{C}$  under reduced pressure, or at room temperature in air.

All powdery samples thus obtained were examined by X-ray diffraction using Mn filtered  $\text{FeK}\alpha$  radiation. The samples consisting only of  $\text{Fe}_3\text{O}_4$ , as revealed by X-ray analysis were further examined by electron microscopic observation, magnetic measurement at room temperature using a vibrating sample magnetometer in magnetic field up to 10 kOe ( $1 \text{ Oe} = 1000/4\pi \text{ A m}^{-1}$ ), BET surface area determination using nitrogen, and chemical analysis. The mean particle size,  $D$ , of  $\text{Fe}_3\text{O}_4$  samples was estimated from the BET surface area ( $\text{m}^2/\text{g}$ ) by assuming that the sample consisted of cubic particles with 5.2 specific gravity. The average particle size,  $d$ , for the samples with  $D < 0.1 \mu\text{m}$  was further estimated from the line broadening of the X-ray diffraction peak for the (311) plane of  $\text{Fe}_3\text{O}_4$  crystal structure.

The cobalt and iron ion contents of samples were determined by atomic absorption after the samples had been dissolved in a HCl solution. The  $\text{Fe(II)}$  content in  $\text{Fe}_3\text{O}_4$  samples was decided by titrating with  $\text{KMnO}_4$  after they had been dissolved in a mixed solution of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

Aqueous suspensions each containing 0.24 M ( $1 \text{ M} = 1 \text{ mol dm}^{-3}$ )  $\text{Fe(II)}$  were prepared by varying  $R$  values in the range 0.3–2.5. On adding a NaOH solution to a  $\text{FeCl}_2$  solution a whitish (or with a tint of blue) precipitate was formed. When the amount of NaOH added fell short of reaching the equivalence point (i.e.,  $R < 1$ ), a bluish white neutral suspension was obtained. When it was equal to or more than that for the equivalence point, a weak or a strongly alkaline suspension was obtained.

When air was bubbled into, a color change took place of a neutral suspension to dark blue. The dark blue precipitates as examined by an X-ray analysis and electronmicroscopy proved to consist of hexagonal plate-like particles with the same

crystal structure as that of green rust I.<sup>2)</sup> When  $R \leq 0.7$ , with the progress of oxidation the formation of a black, ferromagnetic precipitate,  $\text{Fe}_3\text{O}_4$ , could be observed in the dark blue suspension with  $\text{pH } 6.0 \pm 0.3$ . For  $R = 0.9$  or  $1.0$ , the formation of  $\text{Fe}_3\text{O}_4$  took place at  $\text{pH } 7.5\text{--}9.0$  in the presence of  $\text{Fe}(\text{OH})_2$  with or without green rust I. As the precipitates of  $\text{Fe}(\text{OH})_2$  and green rust I completely transformed themselves into  $\text{Fe}_3\text{O}_4$ , the pH sharply dropped to 4 or less. The white precipitate ( $\text{Fe}(\text{OH})_2$ ) in the alkaline suspensions was observed to gradually change without the formation of green rust I to the black, and ferromagnetic precipitate.

It has been found that (a) all the filtered  $\text{Fe}_3\text{O}_4$  samples in a muddy form has the lattice constant,  $a_0$ , nearly constant at  $8.38 \text{ \AA}$ , irrespective of  $R$  values, (b) the dried samples prepared for  $R \geq 1.1$  consist of cubic particles with  $0.2\text{--}0.8 \mu\text{m}$  in size, with  $8.37\text{--}8.38 \text{ \AA}$  in  $a_0$  and contain  $\text{Fe(II)}$  30–31% of the entire  $\text{Fe}$  ions, whereas (c) those for  $R \leq 1$  consist of spherical and cubic particles with  $0.05\text{--}0.15 \mu\text{m}$  in size, with  $8.36 \text{ \AA}$  in  $a_0$  containing  $\text{Fe(II)}$  26–27%.

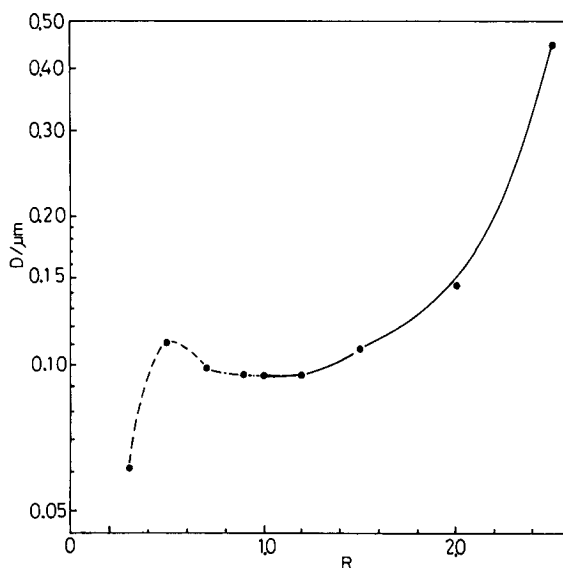


Fig. 1. Mean particle size,  $D$ , of  $\text{Fe}_3\text{O}_4$  samples prepared by oxidation of suspensions with various  $R$  values containing  $0.24 \text{ M FeCl}_2$ . Transformation into  $\text{Fe}_3\text{O}_4$  by oxidation took place in the presence of green rust I (---), a mixture of green rust I and  $\text{Fe}(\text{OH})_2$  (— · —), or  $\text{Fe}(\text{OH})_2$  (—).

A plot of  $D$  values of  $\text{Fe}_3\text{O}_4$  samples thus obtained *vs.*  $R$  values (Fig. 1) demonstrates that the  $D$  values are affected by the  $\text{Fe}(\text{OH})_2$  concentration in the starting suspension when  $R \leq 0.7$ , and that increasing the concentration of an excess  $\text{NaOH}$  accelerates the growth of  $\text{Fe}_3\text{O}_4$  particles (Fig. 2) as a result of retardation in the speed of  $\text{Fe}_3\text{O}_4$  formation caused by oxidation.

Three kind suspensions with  $R = 0.5, 0.9$ , and  $1.5$ , varying in the  $\text{Fe(II)}$  concentration in the range of  $0.046\text{--}0.48 \text{ M}$  were prepared from solutions of  $\text{FeCl}_2$  and

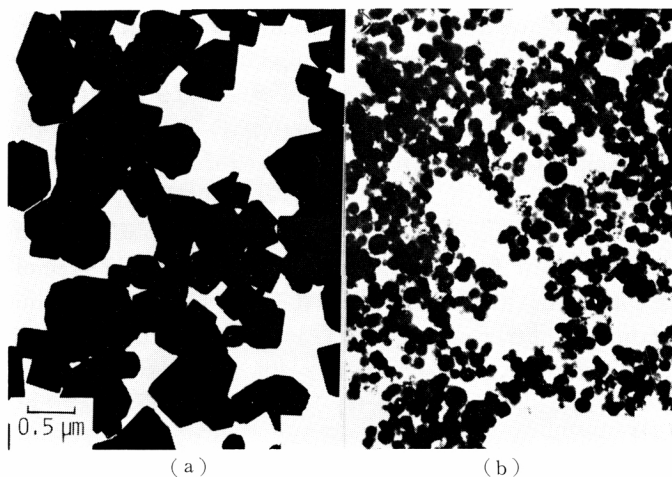


Fig. 2. Electronmicrographs of  $\text{Fe}_3\text{O}_4$  prepared by oxidation of suspensions containing 0.24 M Fe(II) with  $R=2.5$  (a), and 1.1 (b).

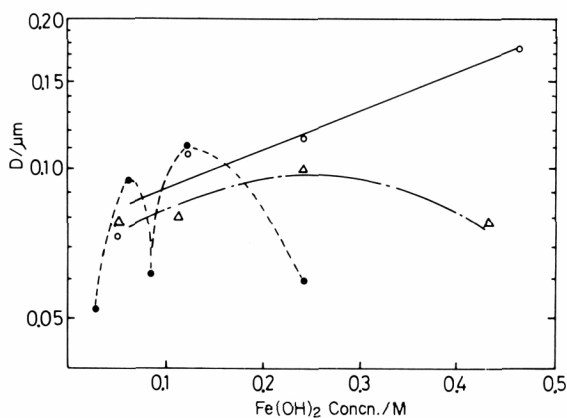


Fig. 3. Mean particle size,  $D$ , of  $\text{Fe}_3\text{O}_4$  prepared by oxidation of suspensions containing different  $\text{Fe(OH)}_2$  concentrations with  $R=0.5$  (●), 0.9 (△), and 1.5 (○).

NaOH, and subjected to oxidation. For the  $R < 1$ , the amount of iron (II) precipitates such as  $\text{Fe(OH)}_2$  increases with increasing  $R$  at a given Fe(II) concentration, and is calculated from  $R$  values. The  $D$  values are plotted against the concentration of  $\text{Fe(OH)}_2$  at three  $R$  values in Fig. 3. The growth of  $\text{Fe}_3\text{O}_4$  particles by oxidation is promoted with increasing the concentrations of both excess NaOH and Fe(II) in the starting suspension.

Similar experiments were conducted at 0.24 M Fe(II) using  $\text{FeSO}_4$  in place of  $\text{FeCl}_2$ . No particular differences could be found in the conditions for promoting the growth of  $\text{Fe}_3\text{O}_4$  particles in alkaline media ( $R \geq 1.0$ ) caused by oxidation. When  $R \leq 0.7$ , fine needle-like  $\alpha\text{-FeO(OH)}$  particles were formed besides cubic  $\text{Fe}_3\text{O}_4$  particles as had been described.<sup>1)</sup>

As has been known, Fe(III) easily reacts with Fe(II) in an alkaline medium to form extremely fine  $\text{Fe}_3\text{O}_4$  particles.<sup>3)</sup> It was found that the presence of such extremely fine  $\text{Fe}_3\text{O}_4$  particles in the starting suspension tends to retard the growth of  $\text{Fe}_3\text{O}_4$  particles caused by oxidation. In order to study the effect of Fe(III) concentration in the starting suspension on the particle growth, alkaline suspensions containing 1.0 M excess NaOH, 0.28 M Fe(II), and different amounts of Fe(III) in the range  $0.046 \leq M \leq 0.260$  were prepared from solutions of  $\text{FeSO}_4$  and  $\text{FeCl}_3$ , and subjected to oxidation.

Table I. Properties of typical  $\text{Fe}_3\text{O}_4$  samples prepared by oxidation at 70°C of suspensions containing 1 M excess NaOH, 0.288 M Fe(II), and different Fe(III) concentrations

Sample	Fe(III)/mol dm <sup>-3</sup>	D/Å	d/Å	Hc/Oe	M/emu g <sup>-1</sup>
A	0.060	322	740	120	65
B	0.102	230	357	95	62
C	0.152	145	236	62	49
D	0.200	129	109	20	44

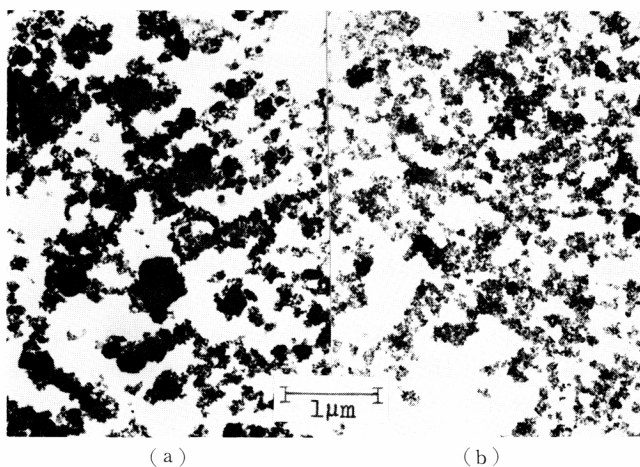


Fig. 4. Electronmicrographs of  $\text{Fe}_3\text{O}_4$  prepared by oxidation of suspensions containing 1 M excess NaOH, 0.29 M Fe(II), and either 0.06 M (a) or 0.15 M Fe(III) (b).

Properties of typical samples are given in Table I, and electron micrographs of typical two  $\text{Fe}_3\text{O}_4$  samples are shown in Fig. 4. The increase in the Fe(III) concentration in the starting suspension up to 0.06 M was found to cause a remarkable decrease in D, but a slight decrease in d. These samples consist of extremely fine particles with 0.01–0.02  $\mu\text{m}$  in size in addition to cubic particles with 0.05–0.1  $\mu\text{m}$  in size (Fig. 4(a)). Further increase in the Fe(III) concentration resulted in the decreases both in D and d.

Their coercivities, Hc, which were independent of the packing densities of cubic  $\text{Fe}_3\text{O}_4$  particles, are plotted against D in Fig. 5. For the samples with  $D > 0.1 \mu\text{m}$  their magnetic saturation values,  $M_s$ , ranging 85–80 emu/g (1 emu/g =  $4\pi \cdot 10^{-7}$  Wb·m

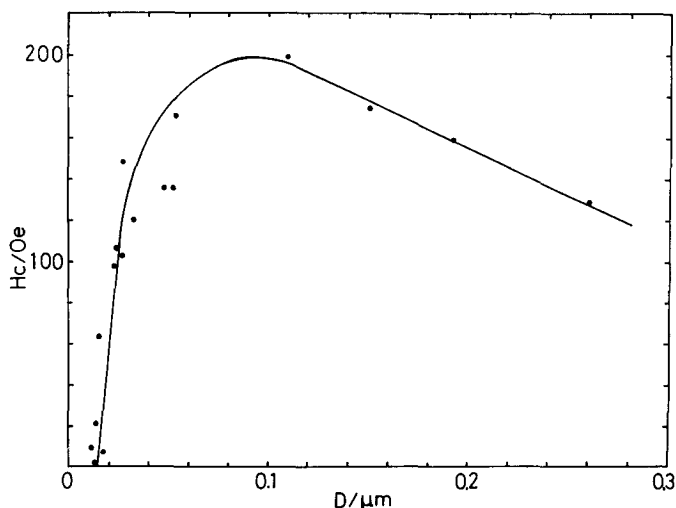


Fig. 5. Coercivity,  $H_c$ , of  $\text{Fe}_3\text{O}_4$  as a function of mean particle size  $D$  of  $\text{Fe}_3\text{O}_4$  samples.

$\text{kg}^{-1}$ ), were independent of  $D$ , whereas their  $H_c$  values increased near to 200 Oe with decreasing  $D$  to  $0.1 \mu\text{m}$  as a result of increasing single-domain particles. Further decrease in  $D$  from 504 to  $119 \text{ \AA}$  causes decreases in  $H_c$  to 13 Oe and in magnetisation,  $M$ , at 10 kOe to 44 emu/g due to an increase in sub-domain (or superparamagnetic) particles.

Alkaline suspensions of hydroxides of Fe(II) and Co(II) in the form of a solid solution of  $\text{Co}_x\text{Fe}_{1-x}/3(\text{OH})_2$  were prepared by adding an excess NaOH to an acidic solution containing  $\text{FeSO}_4$  and  $\text{CoSO}_4$  in the Co(II)/Fe(II) ratios of 0.016 and 0.071, and subjected to oxidation.  $D$  values of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples with  $x=0.05$  and 0.20 could be controlled in the range  $0.1 \leq D \leq 0.5 \mu\text{m}$  by selecting conditions similar to those for promoting the growth of  $\text{Fe}_3\text{O}_4$  particles. As has been known, the difference in the lattice constant between  $\text{Fe}_3\text{O}_4$  and cobalt ferrite is appreciably small. The fine particles with the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  composition ( $x \leq 0.2$ ) could be also prepared by epitaxial coating of cobalt ferrite on the extremely fine  $\text{Fe}_3\text{O}_4$  particles in an alkaline medium.

The  $H_c$  values of typical  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples with three  $D$  values prepared by

Table II. Magnetic properties of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  precipitates prepared under various conditions

Sample	Co(II)+Fe(II)/mol $\text{dm}^{-3}$	R	$D/\mu\text{m}$	$x$	$H_c/\text{Oe}$	$M/\text{emu g}^{-1}$
E	0.360	2.5	0.45	0.20	266	85
F	0.360	1.1	0.12	0.20	633	83
G	0.098	2.5	0.025	0.20	205	75
H	0.360	1.1	0.10	0.05	250	83
I	0.098	2.5	0.025	0.05	175	76

Samples G and I prepared at 0.29 M excess NaOH in the presence of  $\text{Fe}_3\text{O}_4$  particles with  $D=0.025 \mu\text{m}$ .

varying the conditions are given in Table II. Samples **G** and **I** given in the table were prepared by subjecting alkaline suspensions containing  $\text{Co}_{y/3}\text{Fe}_{1-y/3}(\text{OH})_2$  and fine  $\text{Fe}_3\text{O}_4$  particles with  $D=0.025\ \mu\text{m}$  and with  $H_c=103\ \text{Oe}$ . The  $\text{Fe}_3\text{O}_4$  particles which had been prepared in the presence of  $\text{Fe(III)}$  in the alkaline suspension by oxidation as mentioned above were used in a slurry form. Samples **G** and **I** consist of 27 vol% of  $\text{Co}_y\text{Fe}_{3-y}\text{O}_4$  with  $y=0.73$  and  $0.18$ , respectively, as a result of calculation. The  $H_c$  values become greater by coating of  $\text{Co}_y\text{Fe}_{3-y}\text{O}_4$  on the  $\text{Fe}_3\text{O}_4$  particles and the increment in  $H_c$  is affected by the Co content. The  $H_c$  increment is presumably due to the participation of a surface magnetic anisotropy as previously described for needle-like particles of  $\gamma\text{-Fe}_2\text{O}_3$ .<sup>4)</sup>

It has been inferred that a  $\text{Co(II)}$  concentration gradient exists within each particle in the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples prepared even in the absence of  $\text{Fe}_3\text{O}_4$  seeds, depending on the oxidation conditions and that  $H_c$  values of the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples with  $D=0.1\ \mu\text{m}$  vary with heat treatment at  $350^\circ\text{C}$  in vacuo as a result of the diffusion of the metal ions in each particle.<sup>5)</sup>

Table III. Coercivity,  $H_c/\text{Oe}$ , of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples subjected to heat treatment in vacuo

Sample	E	F	G	H	I
250°C	—	930	450	290	240
350°C	280	1500	670	350	260

Five samples **E–I**, each enclosed in glass tubes under reduced pressure of  $10^{-3}$  Pa were heat treated at temperatures between  $250$  and  $350^\circ\text{C}$  for 5 h and then allowed to cool to room temperature. The  $H_c$  values of the samples except for sample **E** begin to increase at  $250^\circ\text{C}$  depending on  $x$  (Table III), whereas no difference in  $M$  values of five samples (**A–E**) was detected before and after heat treatment.

The  $H_c$  value of sample **E** was found to increase at  $560\ \text{Oe}$  with heat treatment at  $200^\circ\text{C}$  in air for 20 h. The  $H_c$  increment with heat treatment must be attributed to the fact that the contribution of the crystal anisotropy of  $\text{Co(II)}$  due to the diffusion of the metal ions in each particle becomes predominant, and the diffusion rate is governed by the concentration of cation vacancies in each particle.

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